

REGULAR ORIGINAL FILING

Application Based on

Docket **85688PAL**
Inventors: Joseph F. Bringley
Customer No. 01333

**COLLOIDAL CORE-SHELL ASSEMBLIES AND METHODS OF
PREPARATION**

Commissioner for Patents,
ATTN: MAIL STOP PATENT APPLICATION
P.O. Box 1450
Alexandria, VA. 22313-1450

Express Mail Label No.: EV 293511490 US

Date: July 18, 2003

**COLLOIDAL CORE-SHELL ASSEMBLIES AND METHODS OF
PREPARATION**

FIELD OF THE INVENTION

5 The invention relates to colloidal dispersions comprising core-shell particles and to methods of forming colloidal core-shell dispersions. In particular, the invention relates to nanoparticles, having either a positive or negative charge, assembled onto the surface of larger colloidal particles, which possess the opposite charge. One, two or more layers of nanoparticles are assembled onto the surface,
10 each layer having a charge opposite that of its adjacent layers.

BACKGROUND OF THE INVENTION

 A dispersion consists of a mixture of small solid particulates in a solvent, such as water. The dispersion is said to be a stable colloid if the solid
15 particulates are sufficiently small and homogeneous such that they do not rapidly aggregate and settle from suspension, usually for a period of many days. Such suspensions are often referred to as “colloids” and are useful in many applications. It is the surface properties of the particulates, such as their electrostatic charge, which is responsible for the stability of colloids. Typically the surfaces are
20 significantly charged, positive or negative, so as to provide electrostatic repulsion to overcome forces which would lead to the aggregation and settling of the colloid. In recent years, it has been of interest to surface modify particles, or to “assemble” colloidal particles of opposite charge to achieve specific properties. However, this is often difficult since the surface modification or assembly disrupts
25 the electrostatic and steric forces necessary for colloidal stability; and stable colloids are not easily obtained.

 Homola et al. in U. S. patent No. 4,280,918 claim “a method of manufacturing a magnetic dispersion containing magnetic particles” whereby a slurry of negatively charged colloidal particles is mixed with a slurry of positively
30 charged magnetic particles, causing the colloidal particles to be attracted to and irreversibly bound to the magnetic particles. The method does not employ

simultaneous addition and typically a sonication step is required to homogenize the product. There is no indication of whether the resulting dispersion is a stable colloid. U. S. patent number 6,417,264 B1 to Kono et al. claims a cationic polymer-modified silica dispersion and a method for its preparation which comprises (1) making a preliminary mixed solution of the silica and cationic polymer and (2) treating this solution with a high pressure homogenizer at a treating pressure of 300 kgf/cm² or more. The method does not employ simultaneous addition of the colloid and surface modifying species. Caruso et al. (J. Amer. Chem Soc. 120, 8523 (1998)) describe a method for preparing nanoparticle-shell multilayers upon larger polystyrene core-particles. A layer-by-layer technique is described in which oppositely charged nanoparticles or polymeric species are sequentially absorbed to the core particle. The technique requires that the core particles be added to a large excess of the shelling polymer or particles and that the unabsorbed fraction (or excess) be removed by repeated centrifugation and wash cycles. Only then is a second shell-layer applied and centrifugation and washing repeated. This method is tedious, requires considerable time and is typically only applicable to dilute (< 5 wt %) systems. In general, previous methods of forming core-shell colloids require purification methods to remove unshelled core particles, or to remove shell particles unassociated (not bound) to the core particles. These methods are time consuming and are not cost effective.

PROBLEM TO BE SOLVED BY THE INVENTION

There remains a need for improved methods of obtaining core-shell colloids which do not require further homogenization and purification, and further provide stable colloids having high concentrations (5 – 50 % solids) and at a high production rate and low cost. There is a further need for improved methods of obtaining well-ordered, homogeneous core-shell colloidal particles in which substantially all of the core particles are shelled, and the colloid is substantially free of unshelled core particles, and is substantially free of shell particles unassociated with the core particles.

SUMMARY OF THE INVENTION

It is an object of the invention to provide methods of obtaining core-shell colloids which do not require further homogenization and purification.

5 It is another object of the invention to provide stable colloids having high concentrations (5 – 50 % solids) and at a high production rate and low cost. It is yet another object of the invention to provide well-ordered, homogeneous core-shell colloidal particles in which substantially all of the core particles are shelled, and the colloid is substantially free of unshelled core particles, and is substantially
10 free of shell particles unassociated with the core particles.

The invention provides a method of forming a colloidal dispersion comprising simultaneously bringing together core particles and shell material in a high shear mixing zone within a dispersion medium to form core-shell particles.

In another embodiment the invention provides a colloidal aqueous
15 dispersion comprising core-shell particles dispersed in an aqueous medium, wherein said aqueous dispersion has a percent solids of greater than 5 weight percent; wherein the solid consists of core-shell particles wherein the surface of said core-shell particles comprises a particulate material and the particulate material is present in an amount sufficient, and only sufficient, to cover the
20 surfaces of all core particles, and the ratio of the average particle diameter of the core particles to the average particle diameter of the particulate material is greater than 4 and wherein said core-shell particle has a zeta potential of greater than ± 30 millivolts.

25 ADVANTAGEOUS EFFECT OF THE INVENTION

The invention provides core-shell colloids at a high production rate and at a low cost, and readily provides colloidally stable dispersions of said core-shell particles. The invention further provides well-ordered, homogeneous core-shell colloidal particles in which substantially all of the core particles are shelled,
30 and the colloid is substantially free of unshelled core particles, and is substantially free of shell particles unassociated with the core particles.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1. shows the experimentally determined (points) and theoretically calculated (line) weight fractions of shell particles necessary to cover the surface of a 100 nm core particle as a function of shell particle size. The figure indicates that the core to shell weight ratios can be accurately described using geometrical relationships.

DETAILED DESCRIPTION OF THE INVENTION

The invention has numerous advantages, providing core-shell colloids at a high production rate and at a low cost, and readily provides colloidally stable dispersions of said core-shell particles. The invention further provides well-ordered, homogeneous core-shell colloidal particles in which substantially all of the core particles are shelled, and the colloid is substantially free of unshelled core particles, and is substantially free of shell particles unassociated with the core particles. These and other advantages will be apparent from the detailed description below.

Colloidal particles find use in a broad variety applications such as pigments for paints, as thickeners and coating aids, in cosmetic products, in paper products, as polishing media in semiconductor electronics, to name only a few. An application of particular importance is the use of colloids in the production of inkjet paper and media. It is often desired to modify the surfaces of colloidal particles to obtain a specific chemical function or to impart a desired physical property to the colloidal particles. Because the surface area of colloidal particles is generally very high, the surface properties play an important role in the application of colloidal particles. Surface modification of colloidal particles may be achieved through the preparation of core-shell particles. Because the shelling species is at the surface, the chemical and physical properties of the core-shell are determined by the nature of the shell species. Thus, core particles may be chosen based upon availability and low cost and can serve as carriers for more expensive and chemically complex shell materials. This approach greatly lowers the cost of

the material, since it may be difficult or even impossible to obtain colloiddally stable shell materials of desired particle size. It is desired that the core-shell colloid be inexpensive, homogeneous and colloiddally stable to facilitate its application in products and devices.

5 Core particle materials may be selected from inorganic materials such as metals, metal oxides, metal oxyhydroxides and insoluble salts; and from organic particulates such as latexes, polystyrene, and insoluble polymers. Preferred core particle materials are inorganic colloiddal particles, such as alumina, silica, boehmite, zinc oxide, calcium carbonate, titanium dioxide, and zirconia. 10 These materials are preferred because of their low cost and general availability. Preferred organic core particle materials are selected from aqueous latexes and polystyrene. In a particularly preferred embodiment of the invention the core particles are silica or aqueous latex particles. In a particularly preferred embodiment of the invention the core particles are silica particles having a 15 diameter between about 50 and 500 nm. These are preferred because of their low-cost and because they are suited to application in inkjet media.

 Shell materials useful for the invention may be selected from organic or inorganic materials including covalently-bonded molecules, polymers, bio-polymers, oxides and particulate materials. The shell material may be chosen 20 to impart a particular property or function to the core-shell particles depending upon the intended use of the core-shell dispersion. In a preferred embodiment of the invention the shell material comprises a bio-molecule or bio-polymer. These are preferred because of their ability to function as bio-medical tools such as in drug-delivery and in bio-recognition. In another preferred embodiment the shell 25 material comprises a hydrolyzable organosilane, which are preferred because of their ability to attach themselves to a wide variety of materials, and because they may impart a specific chemical function to the core-shell particles. In another preferred embodiment said shell material comprises at least one member selected from the group consisting of silica, alumina, zirconia, tin oxide and titania. These 30 oxides are preferred because of their availability and low cost. In the case in which the shell material comprises a particulate, it is preferred that the average

size of the shell particles be less than about 100 nm, and more preferably less than about 50 nm.

The dispersion medium for carrying out the invention may be either aqueous or non-aqueous. Examples of solvents suitable for carrying out the method of the invention include water, methanol, ethanol, iso-propanol, butanol, acetone, methylene chloride, chloroform, benzene or toluene. In a preferred embodiment of the invention the dispersion medium comprises water. Water is preferred because it is inexpensive and environmentally safe.

In the invention, the core and shell dispersions are brought together simultaneously into a high shear mixing zone within a dispersion medium. The high shear mixing zone may be provided by a propeller-like mixer, a static mixer, in-line mixers, dispersators, or other high shear mixing apparatus. The mixing efficiency of the apparatus is dependent upon the type of mixing method chosen and the precise geometry and design of the mixer. For propeller-like mixers the mixing efficiency may be approximated by the turnover rate, where the turnover rate is the stir rate (rev/sec.) times the turnover volume (ml/rev)) divided by the aqueous volume. For in-line or static mixers, the mixing efficiency may be approximated by multiplying the sum of the addition rates of the colloidal dispersions by the turnover volume of the mixer. In each case, the mixing efficiency has units of turnovers/sec. It is preferred that the mixing efficiency be greater than about 0.10 turnovers/sec, and preferably greater than 0.5 turnovers/sec and most preferably greater than 1 turnover/sec. Complete mixing of the two particle dispersion streams is preferably accomplished in less than about 10 seconds; and is more preferably accomplished substantially instantaneously. High turnover rates and fast mixing are preferred because they result in more complete shelling and more stable core-shell colloids.

The core-shell dispersion of the invention is a stable colloid and hence should remain in suspension for a period of greater than a few hours, and more preferably greater than a few days; and most preferably greater than a few weeks. This is preferred because it increases the shelf-life of the colloid. For aqueous core-shell colloids the zeta potential of the dispersion should have a

maximum value greater than about ± 20 mV, and more preferably greater than about ± 30 mV. A high zeta potential is preferred because it increases the colloidal stability of the colloid. The pH of the dispersion may be adjusted as is necessary to obtain a stable colloid. In a preferred embodiment of the invention, the pH of the core-shell, colloidal dispersion is substantially the same as the pH of the aqueous shell material dispersion used to prepare it. This is preferred because it typically maximizes the colloidal stability of the resulting core-shell dispersion. The colloid stability may also be enhanced through the addition of dispersing aids, surfactants, or peptizers.

The core and shell material may be brought together into the high shear mixing zone as dry solids, or be carried in a suspending medium such as a liquid or gas. In a particular preferred embodiment of the invention the core and shell materials are suspended in water and thereafter brought together into the mixing zone. Aqueous suspensions are preferred because they are readily available and inexpensive. The solids concentration of the suspensions may vary from about 0.1 % to about 50 %, but is preferably greater than 1 % and more preferably greater than 5 % and most preferably greater than 10 %. Colloids with higher solids concentrations are preferred because they lower the cost of the resulting core-shell dispersion.

In a preferred embodiment of the invention the core-shell dispersion is recovered in the medium, and thereafter is simultaneously brought together with a second layer shell material in a high shear mixing zone within a dispersion medium to form core-shell particles having two layers. This process may be repeated many times until three or more shell layers are assembled onto the core particle surfaces.

In a particularly preferred embodiment of the invention the shell materials are brought together with the core particles in an amount sufficient, and only sufficient, to substantially cover all the surfaces of said core particles. This is preferred because when there is insufficient coverage, stable core-shell colloids are not obtained. It is furthermore preferred that the shell material should not be supplied into the mixing zone in an excess of that required to substantially cover

all the surfaces of said core particles. In this case, excess shell materials are not strongly bound by the core and may reside as distinct particles in the dispersion. These particles are harmful since they may have properties distinct from the core-shell particles; and purification and separation of these particles from the core-shell may be difficult. A measure of the degree of shelling is approximated by comparing the total projected surface area of the shelling particles to the total surface area of the core particles. It is preferred that the ratio of the total projected surface area per unit mass $[(1/4\pi d^2)/g]$ of shelling particles, to the total surface area of the core particles per unit mass $(\pi d_c^2/g)$, where d_c = diameter of the core particles) be between about 0.7 and 1.5, and more preferably between about 0.8 and 1.2. This is preferred because it gives homogeneous, stable colloids which have a low percentage of unshelled core particles, or conversely, a low percentage of unassociated shelling particles.

In a particular embodiment the invention comprises a colloidal aqueous dispersion comprising core-shell particles dispersed in an aqueous medium, wherein said aqueous dispersion has a percent solids of greater than 5 weight percent; wherein the solid consists of core-shell particles, wherein the surface of said core-shell particles comprises a particulate material and the particulate material is present in an amount sufficient to cover the surfaces of all core particles, and the ratio of the average particle diameter of the core particles to the average particle diameter of the particulate material is greater than 4. It is preferred that the diameter of the core be at least 4 times greater than the diameter of the shell particle, since stable core-shell colloids are not obtained for diameter ratios less than four.

The following examples illustrate the practice of this invention. They are not intended to be exhaustive of all possible variations of the invention. Parts and percentages are by weight unless otherwise indicated. A stable colloid as referenced in the examples is defined as a particulate suspension in which there is no evidence for aggregation of core particles as determined by particle size measurement, and that there is not visible flocculation or settling of the colloid for at least one week after its preparation. Significant growth of average particle size

to diameters greater than about three times the core diameter, and visible settling of the colloid within one week of its preparation is indicative of an unstable colloid.

5

EXAMPLES

Materials

Boehmite, $\text{AlO}(\text{OH})$, was purchased under the trade name Catapal 200®, from Sasol North America Inc. Dispersions of Catapal 200® in distilled water were made at a solids content of 10 – 35 % (weight/weight); the dispersion had a mean particle size of about 85 nm (nm = nanometer, where 1 nm = 10^{-9} m), pH of 3.4 – 3.8, and specific gravity from about 1.1 – 1.3 g/ml. Silica colloids of varying size were obtained from Nalco Chemical Company and nanoparticle Zirconia from Nyacol. Fumed silica and fumed alumina were obtained from Cabot Corporation.

15

Material	Chemical composition	core or shell material	particle size (nm)	pH	particle charge
Catapal 200®	$\text{AlO}(\text{OH})$	core	100	3.6	positive
Cabot PG003®	Al_2O_3	core	230	3.8	positive
Cabot PG001®	fumed- SiO_2	core	250	10.0	negative
Nalco 2329®	SiO_2	core	90	9-10	negative
Nalco 1115®	SiO_2	shell	4	10.5	negative
Nalco 1130®	SiO_2	shell	8	10.0	negative
Nalco 1140®	SiO_2	shell	15	9.7	negative
Nalco 1050®	SiO_2	shell	20	9.0	negative
Nyacol ZrO_2 ®	ZrO_2	shell	5-10	3.8	positive
sylojet A200®	$\text{Al}_2(\text{OH})_5\text{Cl}$	shell	5-10	3.6	positive
$\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$	$\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$	shell	2 nm*	10	

*material is likely molecular or oligomeric in nature.

Table 1. Physical properties are given for the colloidal dispersions used as materials for core/shell experiments.

5 Core/shell colloidal dispersions were prepared by the simultaneous addition of the core and the shell colloidal dispersions into a highly efficient mixing apparatus. The colloidal dispersions were introduced via calibrated peristaltic pumps at known flow rates. The mixing efficiencies and flow rates were varied to obtain stable core/shell colloidal dispersions. The details of the
10 preparation and the characteristics of the dispersions are given below. The mixing efficiency of the apparatus is described by the turnover rate, where the turnover rate = (stir rate(rev/min) x turnover volume (ml/rev)) divided by the aqueous volume. The mixing efficiency typically was kept constant for each example and was about 25 turnovers/min, or 0.4 turnovers/sec. Electrophoretic mobility
15 measurements were made using a Zeta-Meter System 3.0+ instrument (Zeta-Meter, Inc). Solutions of the core/shell materials (0.010 w/v%) were prepared using deionized distilled water. The pH was adjusted using 0.1M HCl or 0.1M KOH. The zeta potential (ζ) of the particles was computed as follows:

$$\zeta = (4\pi\eta u_E)/D$$

20 where η = the viscosity of the medium, u_E = electrophoretic mobility of the particle and D = the dielectric of the medium.

Example and Comparative examples. (boehmite/silica core/shell assemblies)

Standard mixing method

25 C-1. 55.3 g of a 30 % (w/w) colloidal dispersion of AlOOH (Catapal 200®) was placed into an erlenmeyer flask and stirred using a magnetic stir bar. To this was added gradually 13.67 g of a 15 % dispersion of 4 nm silica (Nalco 1115). The suspension immediately agglomerated strongly and after about 3 minutes a viscous liquid paste formed. Upon standing, after 24 hours the
30 dispersion had settled indicating that it was not a stable colloid. The properties of the mixture are summarized in Table 2

Simultaneous Addition

C-2. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2000 rpm was simultaneously
5 added, a 10 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 10.00 ml/min and a 1 % (w/w) dispersion of silica (Nalco 1115®) at a rate of 6.3 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 94.1 % boehmite and 5.9 % silica. The resulting dispersion had a bimodal particle size distribution with populations centered at about 0.250 microns and about 4.0
10 microns; and settled after standing, indicating that the dispersion was not a stable colloid. The properties of the resulting mixture are summarized in Table 2.

I-1. This was prepared in an identical manner to that of I-1, except that the 1 % silica colloid was added at a rate of 8.9 ml/min. The weight ratio of
15 the resulting colloid was 93.0 % boehmite and 7.0 % silica. The resulting dispersion had a particle size of 110 nm and did not settle after standing, indicating that the dispersion was a stable colloid. The properties of the resulting colloidal assembly are summarized in Table 2.

I-2. This was prepared in an identical manner to that of I-1, except that the 1 % silica colloid was added at a rate of 11.8 ml/min. The weight ratio of
20 the resulting colloid was 90.9 % boehmite and 9.1 % silica. The resulting dispersion had a particle size of 110 nm and did not settle after standing, indicating that the dispersion was a stable colloid. The zeta potential of the
25 colloidal particles was found to be about -40 mV at a pH of about 7.0, indicating that the particles were negatively charged. The properties of the resulting colloidal assembly are summarized in Table 2.

I-3. This was prepared in an identical manner to that of I-1, except
30 that the 1 % silica colloid was added at a rate of 13.2 ml/min. The weight ratio of the resulting colloid was 89.0 % boehmite and 11.0 % silica. The resulting

dispersion had a particle size of 120 nm and did not settle after standing, indicating that the dispersion was a stable colloid. The zeta potential of the colloidal particles was found to be about -35 mV at a pH of 8.0 indicating that the particles were negatively charged. The properties of the resulting colloidal assembly are summarized in Table 2.

I-4. This was prepared in an identical manner to that of I-1, except that the 1 % silica colloid was added at a rate of 21.0 ml/min. The weight ratio of the resulting colloid was 84.4 % boehmite and 15.6 % silica. The resulting dispersion had a particle size of 130 nm and did not settle after standing, indicating that the dispersion was a stable colloid. The properties of the resulting colloidal assembly are summarized in Table 2.

I-5. This was prepared in an identical manner to that of I-1, except that the 1 % silica colloid was added at a rate of 29.8 ml/min. The weight ratio of the resulting colloid was 80.6 % boehmite and 19.4 % silica. The resulting dispersion had a particle size of 120 nm and did not settle after standing, indicating that the dispersion was a stable colloid. The properties of the resulting colloidal assembly are summarized in Table 2.

20

I-6. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 3000 rpm was simultaneously added, a 30 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 35.0 ml/min and a 15 % (w/w) dispersion of silica (Nalco 1115®) at a rate of 6.8 ml/min, for 25 minutes. The weight ratio of the resulting colloid was 91.0 % boehmite and 9.0 % silica. The resulting dispersion was 23.4 % solids by weight, had a particle size of 90 nm, pH = 9.5, and did not settle after standing, indicating that the dispersion was a stable colloid. The zeta potential of the colloidal particles was found to be about -30 mV at a pH of 8.0 indicating that the particles were negatively charged. The properties of the resulting colloidal assembly are summarized in Table 2.

30

C-3. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2000 rpm was simultaneously added, a 10 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 10.00
5 ml/min and a 2 % (w/w) dispersion of 8 nm silica (Nalco 1130®) at a rate of 6.0 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 89.9 % boehmite and 10.1 % silica. The resulting dispersion had a bimodal particle size distribution with populations centered at about 0.40 microns and about 4.0 microns; and settled after standing, indicating that the dispersion was not a stable
10 colloid. The properties of the resulting mixture are summarized in Table 2.

I-7. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2000 rpm was simultaneously
15 added, a 10 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 10.00 ml/min and a 2 % (w/w) dispersion of 8 nm silica (Nalco 1130®) at a rate of 9.5 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 84.9 % boehmite and 15.1 % silica. The resulting dispersion had an average particle size distribution of 120 nm; and did not settle after standing, indicating that the
20 dispersion was a stable colloid. The properties of the resulting colloidal assembly are summarized in Table 2.

I-8. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2000 rpm was simultaneously
25 added, a 10 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 10.00 ml/min and a 2 % (w/w) dispersion of 8 nm silica (Nalco 1130®) at a rate of 11.0 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 83.2 % boehmite and 16.8 % silica. The resulting dispersion had an average particle size distribution of 110 nm; and did not settle after standing, indicating that the
30 dispersion was a stable colloid. The properties of the resulting colloidal assembly are summarized in Table 2.

C-4. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2000 rpm was simultaneously added, a 10 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 10.00
5 ml/min and a 5 % (w/w) dispersion of 15 nm silica (Nalco 1140®) at a rate of 2.3 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 90.1 % boehmite and 9.9 % silica. The resulting dispersion had an average particle size distribution of about 4.0 microns; and settled after standing, indicating that the dispersion was not a stable colloid. The properties of the resulting mixture are
10 summarized in Table 2.

C-5. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2000 rpm was simultaneously added, a 10 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 10.00
15 ml/min and a 5 % (w/w) dispersion of 15 nm silica (Nalco 1140®) at a rate of 5.3 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 79.6 % boehmite and 20.4 % silica. The resulting dispersion had an average particle size distribution of about 0.40 microns; and settled after standing, indicating that the dispersion was not a stable colloid. The properties of the resulting mixture are
20 summarized in Table 2.

I-9. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2000 rpm was simultaneously added, a 10 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 10.00
25 ml/min and a 5 % (w/w) dispersion of 15 nm silica (Nalco 1140®) at a rate of 7.0 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 74.6 % boehmite and 25.4 % silica. The resulting dispersion had an average particle size distribution of about 0.30 microns; and did not settle after standing, indicating that the dispersion was a stable colloid. The properties of the resulting colloidal
30 assembly are summarized in Table 2.

I-10. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 3000 rpm was simultaneously added, a 34.2 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 20.00 ml/min and a 40.0 % (w/w) dispersion of 15 nm silica (Nalco 1140®) at a rate of 5.3 ml/min, for 40 minutes. The weight ratio of the resulting colloid was 69.8 % boehmite and 30.2 % silica. The resulting dispersion had an average particle size distribution of about 100 nm microns; and did not settle after standing, indicating that the dispersion was a stable colloid. The properties of the resulting colloidal assembly are summarized in Table 2.

10

C-6. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2000 rpm was simultaneously added, a 10 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 10.00 ml/min and a 5 % (w/w) dispersion of 20 nm silica (Nalco 1050®) at a rate of 5.2 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 79.7 % boehmite and 20.3 % silica. The resulting dispersion had an average particle size distribution of about 1.0 microns; and settled after standing, indicating that the dispersion was not a stable colloid. The properties of the resulting mixture are summarized in Table 2.

20

C-7. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2000 rpm was simultaneously added, a 10 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 10.00 ml/min and a 5 % (w/w) dispersion of 20 nm silica (Nalco 1050®) at a rate of 7.0 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 74.4 % boehmite and 25.6 % silica. The resulting dispersion had an average particle size distribution of about 0.5 microns; and settled after standing, indicating that the dispersion was not a stable colloid. The properties of the resulting mixture are summarized in Table 2.

25

I-11. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2000 rpm was simultaneously added, a 10 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 10.00 ml/min and a 5 % (w/w) dispersion of 20 nm silica (Nalco 1050®) at a rate of 9.0 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 69.5 % boehmite and 30.5 % silica. The resulting dispersion had an average particle size distribution of about 340 nm; and settled only very very slowly upon standing. These results indicate that the dispersion is intermediate in colloidal stability. The properties of the resulting colloidal assembly are summarized in Table 2.

Table 2.

<u>Ex. or Comp.</u> <u>Ex.</u>	<u>Shell particle</u>	<u>weight %</u> [shell/(core + shell)]	<u>Particle Size (nm)</u>	<u>Stable Colloid</u>
C-1	4 nm silica	11	N.A.	No
C-2	4 nm silica	5.9	250	No
I-1	4 nm silica	7.0	110	Yes
I-2	4 nm silica	9.1	110	Yes
I-3	4 nm silica	11.0	120	Yes
I-4	4 nm silica	15.6	130	Yes
I-5	4 nm silica	19.4	120	Yes
I-6	4 nm silica	9.0	90	Yes
C-5	8 nm silica	10.1	4000	No
I-7	8 nm silica	15.1	120	intermediate
I-8	8 nm silica	16.8	110	Yes
C-6	15 nm silica	9.9	4000	No
C-7	15 nm silica	20.4	400	No
I-9	15 nm silica	25.4	300	Yes
I-10	15 nm silica	30.2	100	Yes
C-8	20 nm silica	20.3	1000	No

C-9	20 nm silica	25.6	500	No
I-11	20 nm silica	30.5	340	intermediate

N.A. particle size not applicable since the dispersion was too viscous to be meaasured.

The data of Table 2 show that the standard mixing method is
5 unable to provide stable core-shell colloidal assemblies even when the shell is
present at a level to sufficiently cover the surface of the core. The data further
show that the successful preparation of stable core/shell assemblies is dependent
upon the ratio of shell to core particles and is dependent upon the size of the shell
particles. The relationship between these factors is shown more clearly in Figure 1
10 in which we plot the experimentally determined weight % shell/(core + shell)
necessary to achieve a stable core-shell colloid (from Table 2 above) versus that
calculated from simple geometrical considerations (see below). The geometrical
considerations simply account for the fact that a given number of shell particles
are required to completely cover the surface of the core particle; and that for larger
15 shell particles this requires a greater weight fraction since the thickness of the shell
increases.

Geometrical considerations:

20 Assume assembly of square-net close-packed shell particles – about 80 % of space
filled by the shell particles.
surface area of sphere = πd^2
projected area of sphere = $\pi d^2/4$
volume of sphere = $\pi d^3/6$

25 then the surface area (S.A.) of the core particles per gram of particles is
S.A. = $[\pi d^2]/\text{volume} \times \text{density} = 6/[d_c \cdot \rho_c]$

and

30 then the projected area (P.A.) of the shell particles per gram of particles is
P.A. = $[\pi d^2/4]/\text{volume} \times \text{density} = 3/2[d_s \cdot \rho_s]$

35 then the ratio of grams of shell particles to cover a gram of core particles is
S.A. core (g/m²)/ P.A. shell g/m²

and upon reduction is

$$\text{ratio} = 4(0.8)[d_s \cdot \rho_s] / [d_c \cdot \rho_c]$$

- 5 where d_s and ρ_s are the diameter and density of the shell particles, respectively; and d_c and ρ_c are the diameter and density of the core particles, respectively.

The weight percent at square-net close packing is a simple expression derived from this and is

10

$$\text{weight \% shell/(core + shell)} = [\text{ratio}/(\text{ratio} + 1)] \times 100 \%$$

for a 100 nm $\text{AlO}(\text{OH})$ core particles having a density $3.1 \text{ g}/10^{-6} \text{ m}^3$ and silica shell particles having a density $2.1 \text{ g}/10^{-6} \text{ m}^3$ we get the following values

15

shell particle diameter	w % shell/core
4 nm	8.0
8 nm	14.8
15 nm	24.5
20 nm	30.2

These values are plotted in Figure 1.

- It can be seen in Fig. 1 that the experimentally determined (points) and theoretically calculated (line) weight fractions of shell particles necessary to cover the surface of a 100 nm core particle as a function of shell particle size. The figure indicates that the core to shell weight ratios can be accurately described using geometrical relationships.

- The data of Figure 1 clearly show that the core-shell assembly process closely follows the geometrical relationships assumed for packing of the shell around the spherical core. These data indicate that stable core/shell assemblies cannot be prepared unless a sufficient number of shell particles are present. From Table 2, once the core is "saturated" with shell particles the particle size no longer increases, or only very slightly, indicating that excess shell particles do not assemble into a second shell layer.

An alternative method of expressing the geometrical relation is arrived at by comparing the total projected surface area of the shelling particles to the total surface area of the core particles. For spherical core and shell particles,

the surface of the core particles will be covered when the ratio of the total projected surface area per unit mass $[(1/4\pi d^2)/g]$ of shelling particles, to the total surface area of the core particles per unit mass $(\pi d_c^2/g)$, where d_c = diameter of the core particles) is equal to one. Because the particles are not ideally spherical and
5 because the packing of shell particles around the core may not be perfectly ordered, the ratio may vary from about 0.8 and 1.2, or may be from about 0.7 to 1.5 if the particles are significantly non-spherical.

Examples and comparison examples (Silica/Zirconia Core/Shell Assemblies)

10 Standard mixing method

C-10. 100.0 g of a Nalco 2329® (40 % colloidal silica) was placed into an erlenmeyer flask and stirred using a magnetic stir bar. To this was added gradually 11.0 g of a 20.0 % dispersion of zirconia. The suspension immediately agglomerated strongly and after about 5 minutes a thick paste formed. After 24
15 hours the dispersion had settled indicating that it was not a stable colloid .

C-11. 100.0 g of Nalco 2329® (40 % colloidal silica) was placed into an erlenmeyer flask and stirred using a magnetic stir bar. To this was added gradually 21.9 g of a 20.0 % dispersion of zirconia. The suspension immediately agglomerated strongly and after about 5 minutes a viscous liquid paste formed.
20 After 24 hours the dispersion had settled indicating that it was not a stable colloid.

Simultaneous Addition Method

I-12. Into a 2.0 L container containing 800 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2700 rpm was simultaneously
25 added a 40 % (w/w) silica colloid core particle (Nalco 2329®) at a rate of 40.00 ml/min, and a 20 % zirconia colloid (Nyacol ZrO₂®) colloid at a rate of 8.0 ml/min, each for 10 minutes. The weight ratio of the resulting colloid was therefore 92.2 % silica and 8.8 % zirconia. The resulting dispersion had a particle size of 120 nm and did not settle after standing, indicating that the dispersion was
30 a stable colloid. The properties of the resulting colloidal assembly are summarized in Table 3.

I-13. Into a 2.0 L container containing 800 ml of distilled water which was stirred with a prop-like stirrer at a rate of 2700 rpm was simultaneously added a 40 % (w/w) silica colloid core particle (Nalco 2329®) at a rate of 40.00 ml/min, and a 20 % zirconia colloid (Nyacol ZrO₂®) colloid at a rate of 12.4 ml/min, each for 10 minutes. The weight ratio of the resulting colloid was therefore 87.0 % silica and 13.0 % zirconia. The resulting dispersion had a particle size of 120 nm and did not settle after standing, indicating that the dispersion was a stable colloid. The properties of the resulting colloidal assembly are summarized in Table 3.

Table 3.

<u>Ex. or Comp. Ex.</u>	<u>Method</u>	<u>Shell particle</u>	<u>weight % [shell/(core + shell)]</u>	<u>Particle Size (nm)</u>	<u>Stable Colloid</u>	<u>Particle Charge</u>
C-10	std. mixing	10 nm ZrO ₂	5.2	> 1000	No	n.m.
C-11	std. mixing	10 nm ZrO ₂	10	> 1000	No	n.m.
I-12	Simul. Add	10 nm ZrO ₂	8.8	120	Yes	pos.
I-13	Simul. Add	10 nm ZrO ₂	13.0	120	Yes	pos.

The data of Table 3 indicate that the standard mixing method is not suitable for preparing stable colloidal assemblies, while the simultaneous addition method readily provides stable core/shell colloidal assemblies.

Examples and comparison examples (boehmite/silica core/shell assemblies)

Standard mixing method

C-12. 50.0 g of a 30 % (w/w) colloidal dispersion of boehmite, AlOOH, (Catapal 200®) was placed in an erlenmeyer flask and stirred vigorously. To this was added 21.6 g of a 30 % dispersion of colloidal silica (Nalco 1140®). The weight percent of shell particles to (core + shell) particles was therefore 30.2 % and the total % percent solids was 30.0 %. The suspension immediately set into a solid mass and agglomerated particles adhered to the sides of the flask. After 24

hours the dispersion had settled and set into a solid mass indicating that it was not a stable colloid.

- C-13. 50.0 g of a 15 % (w/w) colloidal dispersion of boehmite, AlOOH, (Catapal 200®) was placed in an erlenmeyer flask and stirred vigorously. To this was added 21.6 g of a 15 % dispersion of colloidal silica (Nalco 1140®). The weight percent of shell particles to (core + shell) particles was therefore 30.2 % and the total % percent solids was 15.0 %. The suspension became very viscous and was difficult to mix but became less viscous with continued mixing.
- 10 The stirring was stopped after about 20 minutes and the dispersion allowed to stand. After about 24 hours, the dispersion had settled producing a solid mass at the bottom of the flask, and indicating that it was not a stable colloid.

- C-14. 50.0 g of a 10 % (w/w) colloidal dispersion of boehmite, AlOOH, (Catapal 200®) was placed in an erlenmeyer flask and stirred vigorously. To this was added 21.6 g of a 10 % dispersion of colloidal silica (Nalco 1140®). The weight percent of shell particles to (core + shell) particles was therefore 30.2 % and the total % percent solids was 10.0 %. The suspension became viscous, but became less viscous with continued mixing. The stirring was stopped after about
- 20 20 minutes and the dispersion allowed to stand. After about 24 hours, the dispersion had settled producing a solid mass at the bottom of the flask, and indicating that it was not a stable colloid.

- C-15. 50.0 g of a 5 % (w/w) colloidal dispersion of boehmite, AlOOH, (Catapal 200®) was placed in an erlenmeyer flask and stirred vigorously. To this was added 21.6 g of a 5 % dispersion of colloidal silica (Nalco 1140®). The weight percent of shell particles to (core + shell) particles was therefore 30.2 % and the total % percent solids was 5.0 %. The stirring was stopped after about 20 minutes and the dispersion allowed to stand. After about 24 hours, the
- 30 dispersion had settled slightly but could easily be re-dispersed with gentle agitation. The average particle size was about 100 nm.

Simultaneous Addition Method

I-14. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 3000 rpm was simultaneously added, a 34.2 % (w/w) dispersion of boehmite (Catapal 200®) at a rate of 20.00 ml/min and a 40.0 % (w/w) dispersion of 15 nm silica (Nalco 1140®) at a rate of 5.3 ml/min, for 40 minutes. The weight ratio of the resulting colloid was 69.8 % boehmite and 30.2 % silica. The resulting dispersion had an average particle size distribution of about 100 nm microns; and did not settle after standing, indicating that the dispersion was a stable colloid. The properties of the resulting colloidal assembly are summarized in Table 4.

Table 4

<u>Ex. or Comp. Ex.</u>	<u>Method</u>	<u>Shell particle</u>	<u>weight % [shell/(core + shell)]</u>	<u>Particle Size (nm)</u>	<u>Stable Colloid</u>	<u>percent solids</u>
C-12	std. mixing	15 nm SiO ₂	30.2	n.m.	No	30
C-13	std. mixing	15 nm SiO ₂	30.2	n.m.	No	15
C-14	std. mixing	15 nm SiO ₂	30.2	n.m.	No	10
C-15	std. mixing	15 nm SiO ₂	30.2	100	Yes	5
I-14	Simul. Add.	15 nm SiO ₂	30.2	100	Yes	30.3

The data of Table 4 indicate that std. mixing may be adequate to prepare core-shell assemblies at dilute concentrations but that the inefficiency of the standard addition and mixing method prevents the formation of stable core-shell colloids at higher concentrations. The assemblies prepared by the method of the invention are stable at very high concentrations.

Examples and comparison examples (Multiple-shell Colloidal Assemblies)

C-16. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 3000 rpm was simultaneously added: the silica surface modified colloid described in I-6 (diluted to 10 % solids by the addition of distilled water) at a rate of 10.0 ml/min, and a 0.5 % (w/w) dispersion of colloidal zirconia at a rate of 5.5 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 88.7 % boehmite, 8.8 % silica (1st shell) and 2.5 % zirconia (2nd shell). The resulting dispersion had an average particle size of 5.7 microns, and settled after standing, indicating that the dispersion was not a stable colloid. The properties of the resulting colloidal assembly are summarized in Table 5.

I-15. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 3000 rpm was simultaneously added: the silica surface modified colloid described in I-6 (diluted to 10 % solids by the addition of distilled water) at a rate of 10.0 ml/min, and a 1.0 % (w/w) dispersion of colloidal zirconia at a rate of 5.7 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 86.3 % boehmite, 8.5 % silica (1st shell) and 5.2 % zirconia (2nd shell) . The resulting dispersion had an average particle size of 131 nm, and did not settle after standing, indicating that the dispersion was a stable colloid. The zeta potential of the colloidal particles was found to be about + 25 mV at a pH of 4.0, indicating that the particles were positively charged and that the sign of the particles had been reversed by the shelling process. The properties of the resulting colloidal assembly are summarized in Table 5.

I-16. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 3000 rpm was simultaneously added: the silica surface modified colloid described in I-6 (diluted to 10 % solids by the addition of distilled water) at a rate of 10.0 ml/min, and a 1.0 % (w/w) dispersion of colloidal zirconia at a rate of 12.0 ml/min, for 10 minutes. The weight ratio of the resulting colloid was 81.8 % boehmite, 8.1 % silica (1st shell) and 10.1 % zirconia colloid (2nd shell) . The resulting dispersion had an average

particle size of 125 nm, and did not settle after standing, indicating that the dispersion was a stable colloid. The zeta potential of the colloidal particles was found to be about + 35 mV at a pH of 4.0, indicating that the particles were positively charged and that the sign of the particles had been reversed by the shelling process. The properties of the resulting colloidal assembly are summarized in Table 5.

I-17. Into a 2.0 L container containing 200 ml of distilled water which was stirred with a prop-like stirrer at a rate of 3000 rpm was simultaneously added: the silica surface modified colloid described in I-6 at a rate of 10.0 ml/min, and 52.0 g of 3-aminopropyl(triethoxy)silane (3APSi) at a rate of about 1.8 ml/min; and 28.8 g of acetic acid at a rate of about 0.9 ml/min, each for 30 minutes. The resulting dispersion was 14.6 % solids and had a pH = 4.7. The weight ratio of the resulting colloid was 74.2 % boehmite, 6.7 % silica (1st shell) and 19.1 % siloxyl(propyl-3-ammonium) acetate (2nd shell) . The resulting dispersion had an average particle size of 490 nm, and did not settle after standing, indicating that the dispersion was a stable colloid. The resulting dispersion was then coated and tested as described above and the results shown in Table 5 below.

Table 5.

<u>Ex. or Comp. Ex.</u>	<u>1st shell particle</u>	<u>2nd Shell material</u>	<u>Core/Shell/shell Ratio (w/w)</u>	<u>Particle Size (nm)</u>	<u>Stable Colloid</u>
C-16	SiO ₂	ZrO ₂	88.7/8.8/2.5	5700	No
I-15	SiO ₂	ZrO ₂	86.3/8.5/5.2	130	Yes
I-16	SiO ₂	ZrO ₂	81.8/8.1/10.1	125	Yes
I-17	SiO ₂	3APSi	74.2/6.7/19.1	490	Yes

The data of Table 5 indicate that the method the invention is suitable for preparing multiple core/shell assemblies provided that a sufficient amount of shell material is provided to substantially cover the surface of the inner core or inner shell layers.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.